THE SYNTHESIS OF HIGHER ALCOHOLS ON Cu/ZnO CATALYSTS PROMOTED WITH K_2CO_3

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Alkali oxides added to methanol catalysts increase the formation of ethanol, n-propanol and isobutyl alcohol. This result has been known for many years, yet few quantitative studies have been reported in the literature. Data obtained on a commercial copper-zinc oxide catalyst promoted with K_2CO_3 are presented and compared with published work. Catalyst particles with a mean diameter of about 0.9 mm were used. The catalyst was initially reduced in $2H_2$ + 1CO gas at 300°C and atmospheric pressure for 12-15 hours. Most of the synthesis tests were made at 285°C and 13.2 MPa of $1H_2$ + 2CO gas. The alkali concentration varied from 0-10 wt % K_2CO_3; the optimum amount was about 0.5% by weight, as shown in Table 1. The H_2 to CO feed ratio was important in determining the higher alcohol selectivity. The rate of production of isobutyl alcohol varied as $p_{H2}^{-0.7}\ p_{CO}^{2.2}$ while for methanol, ethanol and n-propanol both exponents were positive and less than 1.6. Decreasing the hydrogen to carbon monoxide ratio from 2 to 0.5 more than doubled the isobutyl alcohol selectivity.

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TABLE 1: PROMOTER CONCENTRATION EFFECTS

Pressure = 13.2 MPa. Temperature = 285°C

Wt.% K_2CO_3	0	0.5	1.0	2.0	3.0	10.0
Inlet space velocity (h^{-1})	4300	3300	3800	4300	4600	2900
H_2:CO in feed	0.44	0.47	0.52	0.49	0.48	0.44
Alcohol selectivities(1)						
methanol	65.8	48.6	61.4	75.7	82.4	81.8
ethanol	6.4	4.8	4.8	3.7	2.6	1.6
2-propanol	1.7	0.8	1.8	1.8	1.4	0.3
1-propanol	5.3	6.7	9.2	8.1	7.0	5.2
1-butanol	2.1	4.0	2.5	1.3	1.1	2.2
2-butanol	0.8	1.5	1.7	1.0	1.3	0.9
2-methyl-1-propanol	10.1	18.8	13.8	7.1	3.8	4.6
pentanols	8.0	14.8	4.8	1.2	0.5	3.4
(H_2+CO) consumption						
$mmol.g_{-2}^{-1}.h^{-1}$	50.5	58.5	68.5	41.5	54.3	16.0
$mmol.m^{-2}.h^{-1}$	1.19	1.61	1.76	1.18	1.66	0.89

(1) selectivity = $\frac{\text{C atoms in alcohol i}}{\text{total C atoms in alcohols}} \times 100\%$

A chain growth scheme for the synthesis of alcohols from carbon monoxide and hydrogen is proposed. The scheme describes the alcohol product distribution, assuming one or two carbon addition at the α- or β-carbon atom of the growing alcohol. Estimates of the distribution parameters were obtained from selectivities measured for a range of operating conditions on a Cu/ZnO catalyst promoted with 0.5% K_2CO_3. Typical data showing the values of growth parameters and the comparison of observed and predicted alcohol yields are given in Table 2. The α-addition is a slow step with a large activation energy (140 kJ/mol) while β-addition is faster and has a smaller activation energy (66 kJ/mol). Large methanol selectivities result from the slow initial α-addition, and large 2-methyl-1-propanol selectivities from α-addition being the only growth step of the 2-methyl-1-propanol intermediate. The rate of chain growth is approximately proportional to the CO partial pressure and the rate of chain termination proportional to the H_2 partial pressure. Addition of alcohols to the synthesis gas resulted in significant increases in the yields of some of the alcohols, consistent with the chain growth scheme.

Two papers have been published on this work, Can. J. Chem. Eng., 61, 40 (1983) and J. Catal., 85, 428 (1984).

Table 2: Predicted and Measured Product Distributions

Pressure 10.4 MPa Temperature 285°C

Feed H_2/CO	0.49	0.93	2.01
Space Velocity (h^{-1})	2900	8200	32000
Conversion %			
(H_2+CO)	39	41	23
CO	28	34	27

Alcohols(1)	measured	predicted	measured	predicted	measured	predicted
methanol	0.6177	0.6313	0.8530	0.8572	0.9610	0.9649
ethanol	0.0536	0.0575	0.0505	0.0512	0.0227	0.0227
2-propanol	0.0046	0.0040	0.0022	0.0022	0.0021	0.0003
1-propanol	0.0643	0.0574	0.0378	0.0357	0.0076	0.0071
1-butanol	0.0224	0.0077	0.0062	0.0007	0.0027	0.0008
2-butanol	0.0111	0.0065	0.0043	0.0029	0.0027	0.0004
2-methyl-1-propanol	0.1484	0.1519	0.0402	0.0414	0.0012	0.0024
pentanols	0.0780	0.0838	0.0059	0.0086	0	0.0015

Estimated growth scheme parameters:

Rate constants:			
α	0.136	0.056	0.015
β	1.986	0.870	0.254
γ	0.170	0.013	0.022

Probabilities:			
h	0.136	0.056	0.015
k	0.665	0.465	0.203
ℓ	0.057	0.007	0.018

(1) selectivity = $\frac{\text{C atoms in alcohol i}}{\text{total C atoms in alcohols}}$